Organotin compounds in technology and industry Alwyn G. Davies

Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK



Professor Davies started working on organic peroxides in 1950, then put the peroxy group onto silicon in 1955. Over the years, this work was extended to the peroxides of other metals, including the first peroxytin compounds in 1962. That required an understanding of basic organotin chemistry, which at that time was fairly fragmentary, and led to a lifetime's interest in the subject. He has published many research papers and reviews in the field, and is the author of two editions of *Organotin Chemistry* and the co-editor of a further recent volume, *Tin Chemistry: Fundamentals, Frontiers, and Applications.*

1. Introduction	181
2. Industrial preparation of organotin compounds	181
3. Stabilisation of PVC	182
4. Production of polyurethanes	183
5. Room temperature vulcanisation of silicone polymers	185
6 Transesterification and related reactions	186
7. Coating glass with tin oxide	188
8. Marine antifouling	189
9. Acknowledgement	190
10. References	190

Organotin compounds find a bigger range of technological and industrial applications than the organic compounds of any other metal. Many of these applications involve catalysis or anticatalysis, often in polymer chemistry, and they have an importance out of all proportion to the tonnage of tin which is used. This article reviews the present standing of the non-biological applications of organostannanes, with an emphasis on the mechanisms of the reactions which are involved.

Keywords: organotin compounds, catalysis, industrial technology

1. Introduction

The three major families of organometallic compounds which find application in technology and industry are those based on aluminium, silicon, and tin.

Alkylaluminium compounds are highly reactive, and their applications depend on their chemical properties as alkylating agents, for example, towards tin tetrachloride in the production of alkyltin compounds.

Organosilicon compounds, on the other hand, find applications which depend more on their physical properties. Carbon–silicon and silicon–oxygen bonds are strong and the polysiloxanes (silicones) are kinetically and thermally stable, resistant to oxidation, hydrolysis, and heat, and are strongly hydrophobic. They find use, for example, as oils, rubbers, resins, sealants, and mould release agents.

Organotin compounds show a more even balance of reactivity and stability. Unlike the organoaluminium compounds, they are usually stable enough to be handled in air, but when they carry suitable functional groups they can take part in a wide variety of reactions, and they are used in the laboratory as reagents for organic synthesis. They are also versatile in their applications in industry and technology, and this is the subject of the present review.

Monoorganotin compounds, RSnX₃, find rather few applications. As catalysts, the diorganotin compounds are usually preferred, but the mono- and di-organo compounds are used in conjunction in PVC stabilisation, and butyltin trichloride is finding increasing use in the vapour phase deposition of an SnO₂ film on glass.

The diorganotin compounds, R₂SnX₂, have a low mammalian toxicity, and are used principally as stabilisers for poly(vinyl chloride), as catalysts for the formation of polyurethanes and polysiloxanes and for a variety of reactions at carboxyl centres, and for the chemical vapour deposition of films of SnO₂. The triorganotin compounds are much more biologically active and have been used in agriculture and wood treatment as pesticides and fungicides, though these uses have diminished in recent years because of concerns about their broader toxicity in the environment.^{1,2} A major use has been in the treatment of hulls of ships to prevent fouling by weeds. This is banned now because of the effect it was having on shellfish and molluscs in bays and coastal waters, but a brief account is included here (Section 8) because of its technological interest and current developments in which the technology is being extended to other metals.

Apart from their use in glass coating (Section 7), the principal current applications of organotin compounds thus are in catalysis or anticatalysis (Sections 3–6), particularly in the plastics industry. The tonnage of the metal which goes into organotin compounds is therefore small compared with that which goes into tin plating or solder, but the benefits which accrue from it are out of all proportion to the amount of tin which is involved.

The previous reviews of the field do not cover developments in the past decade, and most emphasise commercial aspects rather than the chemistry which underlies the applications and which is highlighted here.³⁻⁶ Two books^{3,4} from the International Tin Research Institute in 1985 give particularly good early surveys of the field.

2. Industrial preparation of organotin compounds⁷

On the industrial scale, organotin compounds are usually prepared by alkylation of $SnCl_4$ with organo-magnesium or -aluminium compounds.

Grignard reagents, RMgX, are prepared from the metal and an alkyl or aryl halide and need large volumes of solvent and are expensive. It is difficult to restrict their reaction with $SnCl_4$ to partial alkylation unless R is very bulky, and the reaction is usually taken to completion to give R_4 Sn [equations (1) and (2)].

$$RX + Mg \xrightarrow{Et_2O} RMgX$$
 (1)

$$4RMgX + SnCl_4 \longrightarrow R_4Sn + 4MgXCl \qquad (2)$$

The tetraalkylstannane is then heated with the appropriate amount of $SnCl_4$ (the Kocheshkov reaction) when redistribution occurs to give the alkyltin chlorides R_nSnCl_{4-n} [equation (3)].

$$R_4Sn \xrightarrow{SnCl_4} R_3SnCl \longrightarrow R_2SnCl_2 \longrightarrow RSnCl_3 (3)$$

Triethylaluminium can be made from aluminium metal, hydrogen and ethylene [equation (4)], and higher alkylaluminium compounds are then made by the Ziegler growth reaction between triethylaluminium and ethylene, which needs no solvent [equation (5)]. Trimethylaluminium, which is strongly dimerised, does not give this reaction, so it is the evennumbered alkylaluminium compounds, *e.g.* n-Bu₃Al and $(n-C_sH_{17})_3Al$ which are readily accessible.

$$AI + 1.5H_2 + CH_2 = CH_2 \xrightarrow{Et_3AI} Et_3AI$$
(4)

$$Et_{3}AI + 3nCH_{2} = CH_{2} \xrightarrow{110 \text{ °C}} [Et(CH_{2}CH_{2})_{n}]_{3}AI \quad (5)$$

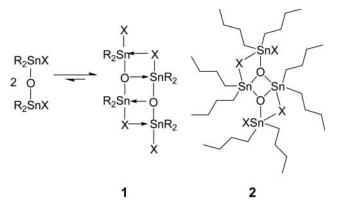
These organoaluminium compounds react with $SnCl_4$ to give the corresponding alkyltin chlorides, and unlike the Grignard reagents, these reactions can be taken to the stage of partial alkylation to give the alkyltin halides directly, *e.g.* equation (6). Dibutyl- and dioctyl-tin dichloride are made industrially by this method.

$$2Bu_3AI + 3SnCl_4 \longrightarrow 3Bu_2SnCl_2 + 2AICl_3 \qquad (6)$$

Other organotin derivatives can then be made from these chlorides. For example, treatment with sodium acetate gives the corresponding organotin acetates, and thiols under basic conditions give the tin thiolates, both of which are used as stabilisers for PVC. Progressive hydrolysis of dibutyltin dichloride gives first the dichlorodistannoxane which is used extensively as a catalyst, and then dibutyltin oxide which is an insoluble polymer [equation (7)].

$$Bu_2SnCl_2 \xrightarrow{H_2O} ClBu_2SnOSnBu_2Cl \longrightarrow (Bu_2SnO)_n(7)$$

These difunctional distannoxanes, XR₂SnOSnR₂X, are ladder-shaped dimers (1) which are highly soluble in non-polar solvents because they have the structure of a reversed micelle (2), with a polar core surrounded by lipophilic alkyl groups,⁸ and they are excellent catalysts for a number of organic reactions apparently because of their nature as binary Lewis acids.



An alternative method of forming the SnC bond was introduced in 1976 by the AKZO company [equations (8) and (9)]. HCl Gas reacts with metallic tin or with SnCl₂ in an ethereal solvent to give the solvated hydrochlorides HSnCl₃ and H₂SnCl₂. These add heterolytically to acrylic esters to give β alkoxycarbonylethyltin compounds [equations (8) and (9)].⁹⁻¹¹

$$Cl_3SnH + CH_2 = CHCO_2R \longrightarrow Cl_3SnCH_2CH_2CO_2R$$
 (8)

$$Cl_2SnH_2 + CH_2 = CHCO_2R \longrightarrow Cl_2Sn(CH_2CH_2CO_2R)_2$$
 (9)

The two reactions can be combined, as shown in equation (10).

Sn + HCl + CH₂=CHCO₂Me
$$\rightarrow$$

98% Cl₂SnCH₂CH₂CO₂Me 96.5%
Cl₂Sn(CH₂CH₂CO₂Me)₂ 3.5%
(10)

Substitution of the chlorine by thioalkyl groups then gives a family of PVC stabilisers (the "estertins") as described below.

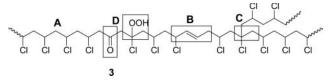
Extensive efforts have been made to prepare organotin compounds by the direct reaction of metallic tin with organic halides, but the only process which as yet has been commercially successful is the preparation of dimethyltin dichloride from methyl chloride and tin in the presence of a catalyst [equation (11)].

$$2\text{MeCl} + \text{Sn} \longrightarrow \text{Me}_2\text{SnCl}_2$$
 (11)

3. Stabilisation of PVC¹²

Poly(vinyl chloride) (PVC) is the third most widely used plastic, after polyethylene and polypropylene, with an annual consumption of about 30 million tonnes, into which go about 75,000 tonnes of organotin stabiliser.¹² The unplasticised (rigid) polymer is used in supply pipes and domestic drainage and in the construction industry in, for example, window profiles and cladding. Plasticised PVC is used in various forms of packaging such as "blister packs", blow-moulded bottles and food wrapping.

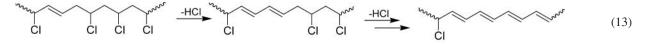
The polymer is prepared by the polymerisation of vinyl chloride, (CH₂=CHCl), in suspension, emulsion, bulk, or solution, by a radical mechanism. The regularity of the (CH₂CHCl)_n chain (**A**) is interrupted by defect sites of unsaturated groups (**B**), branches (**C**), and oxidised structures (**D**), as illustrated in formula **3**.¹³



The unplasticised polymer has a high melting point, and in making PVC sheet, the polymer is calendered between rollers heated to about 200 °C. Pipes and other profiles are made by extrusion, and bottles by blow moulding. Under these conditions, HCl is eliminated starting from the defect sites, particularly the unsaturated positions which typically are present to the extent of about 1 per 1,000 monomer units. The liberated HCl catalyses further elimination, perhaps by the mechanism shown in equation (12).

$$\begin{array}{c} CH - CH \\ H \\ CI - H \end{array} \xrightarrow{CH - CH} CH = CH \\ H \\ CI - H \\ CI - H \end{array} \xrightarrow{CH - CH} (12)$$

This progresses along the chain in a zipper fashion, to give an extended conjugated polyene [equation (13)] which absorbs



in the UV-visible region. The clear polymer develops a yellow, then brown, then black colour, and it becomes brittle. The problem is still present, but less acute, with plasticised PVC which can be processed at a lower temperature.

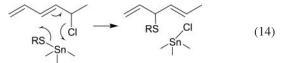
Aerobic oxidation also occurs, initiated in part at carbon radical sites where the chain is sheared by mechanical stress during calendering, and this accelerates HCl elimination.

Organotin compounds have been used as stabilisers to prevent this degradation since 1940.^{14,15} The first commercially successful stabilisers were dibutyltin dilaurate (**4**), dibutyltin maleate (**5**), and dibutyltin methyl maleate (**6**). The most effective are the Sn-S bonded compounds such as dibutyltin di(isooctyl mercaptoacetate) (**7**, R = Bu), usually referred to as isoctyl thioglycollates (IOTGs), for non-food applications. For food-grade PVC, dimethyltin and dioctyltin di(isooctyl mercaptoacetate) (**7**, R = Me or octyl) and di(isooctyl mercaptopropionate) (**8**) and the "estertins" [**9**; see equations (8) and (9)] are used. Dialkyltin derivatives of mercaptoethyl esters, such as the oleate (**10**) have recently been commercialised; as the ester group is inverted from the position which it has in compounds such as **5** and **6**, these are known as "reverse esters".

Typically the loading of the stabiliser is 0.5–2% by weight of the polymer. With the optimum choice of organotin stabiliser stability is conferred on the PVC, both short-term during processing, and subsequent long-term use, and the resulting polymer is clear and colourless.

Choice of the size of the alkyl groups in the stabiliser depends on the relative toxicity (octylSn < methylSn < butylSn for the isooctyl thioglycolates), the solubility in the unplasticised or plasticised polymer which determines the clarity of final product, the compatibility with other components (lubricants, plasticisers, fillers, pigments), the protection which they confer against oxidation and photolytic degradation, and the leachability into fatty foodstuffs.

The primary mechanism of stabilisation appears to be two-fold.¹⁶⁻¹⁹ First, the organotin compound reacts at the allylic defect sites in the polymer, to replace Cl by an alkylthiyl group which is less prone to undergo elimination [equation (14)].

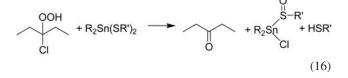


The second effect is to remove the HCl [equation (15)] which otherwise catalyses the elimination.²⁰

$$R_2Sn(SR)_2 + HCI \longrightarrow R_2Sn(SR)CI + HSR (15)$$

Hydroperoxides (\mathbf{D} in formula 3) are reduced by the mercapto groups [equation (16)] and the thiolates confer a

long-term protection against aerobic oxidation presumably by trapping the alkylperoxyl radical, perhaps by its reaction at the tin centre.



The maleate stabilisers operate in part by stopping, by a Diels–Alder reaction, elimination proceeding beyond the diene stage [equation (17)].

$$\begin{array}{c} & \overset{i_{2}}{\xrightarrow{}} & \overset{i_{$$

The maleates do not protect against degradation resulting from oxidation, but they and the estertins do confer stability against photolytic damage, which the thiolates do not. A mixture of stabilisers, which may include phenolic antioxidants and hydroxybenzophenone photo-stabilisers, is therefore frequently used.

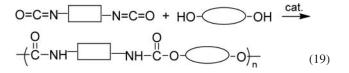
Monoalkyltin trithiolates are more effective than the ditholates in removing allylic halogen [equation (12)], but they cannot be used alone as stabilisers because the alkyltin trichlorides which are formed during that reaction are strong Lewis acids which catalyse further elimination of HCl. The trithiolates are therefore used in mixture with the dithiolates, when ligand exchange regenerates the trithiolates and gives the dichlorides which are weaker, non-catalytic, Lewis acids [equation (18)].

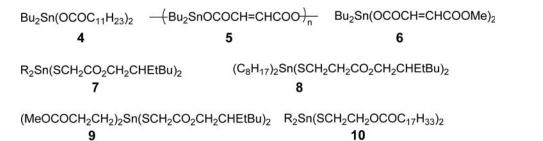
 $2RSnCl_3 + 3R_2Sn(SR')_2 \longrightarrow 2RSn(SR')_3 + 3R_2SnCl_2 (18)$

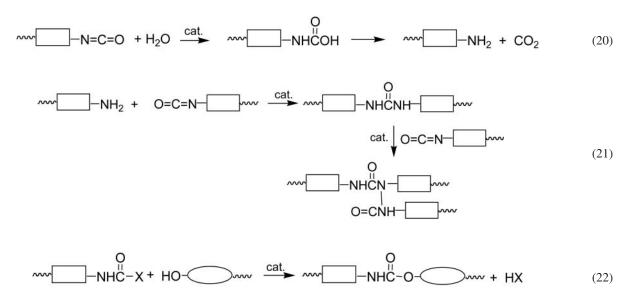
4. Production of polyurethanes²¹

Polyurethanes are used as mouldings, coatings, fibres, adhesives, sealants, elastomers, and soft or rigid foams, in products such as refrigerators, car parts, shoes, building insulation, mattresses, carpet underlays, furniture cushioning, paints, and varnishes. World production in 2007 was about 12 million tonnes.

Linear polyurethanes are usually prepared by the reaction between a diisocyanate and a diol in the presence of a catalyst [equation (19)].

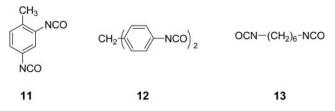




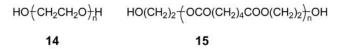


Cross-links are introduced by the incorporation of some triol such as glycerol. If water is present, hydrolysis of the isocyanate generates carbon dioxide [equation (20)] which blows the polymer into a foam. The amine which is also formed then goes on to give a urea link in the polymer chain and further reaction of the isocyanate at the urea moiety may give a biuret cross-link [equation (21)]; alternatively, a blowing agent such as such as CO_2 , a hydrocarbon, or a fluorohydrocarbon may be passed into the polymerising mixture to create the foam.

Typical isocyanates which are used are toluene 2,4-diisocyanate (11), bis(4-isocyanatophenyl)methane (12), and hexamethylene diisocyanate (13).



The diols may typically be based on polyethylene oxide (14) or polypropylene oxide, or a diester-diol co-oligomer, *e.g.* 15.



An alternative approach is to use a "screened" isocyanate in which a reagent HX has been added to the isocyanate [equation (22)]; typical screening agents are phenols, oximes, caprolactam and 3,4-dimethylpyrazole. In the polymerisation process, HX is replaced by the diol. These screened isocyanates are used particularly in coatings. This process has been thoroughly reviewed by Wicks.²²

By either method, organotin compounds are used to catalyse the formation of the polyurethane; dibutyltin dilaurate is very commonly used. Table 1 shows the relative rates of the model reaction of phenyl isocyanate with methanol in the presence of some organotin catalysts.

In injection moulding, the diol and diisocyanate, containing the catalyst and other components, are injected into the mould and cured. The rate of cure determines the turn-round rate of the process.

The manufacture of a foam involves sophisticated technology. The diisocyanate, diol, and catalyst are mixed, together with any necessary filler, cross-linking polyol, antioxidant, blowing agent, or surfactant (to stabilise the foam) and the

Table 1 Relative rates of reaction of phenyl isocyanate and methanol in the presence of organotin catalysts

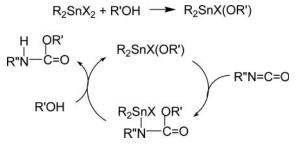
	-
Catalyst	Relative rate
None	1
Bu_SnCl_	200
Bu ₂ SnCl ₂ Bu ₂ Sn(OCOMe) ₂	30,000
(Buẩ,SnO)	40,000
(Bu ₂ SnO) Bu ₂ Sn(OCOC ₁₀ H ₂₁) ₂	56,000

foam is extruded from the reactor as a continuous block; obviously, the balance between the rates of blowing the foam and the setting of the foam is crucial and governs the choice of the catalyst.

Organic coatings, sealants, and adhesives usually involve aliphatic isocyanates. A one-component formulation might consist of an isocyanate-terminated prepolymer (low polymer) and catalyst in a solvent such as toluene. On exposure to air the solvent evaporates to leave a film and curing is brought about by moisture which joins the chains through urea linkages as in equations (20) and (21). A heat-cured paint may use a blocked urethane.

Two basic mechanisms have been proposed for the formation of the urethane linkage from the isocyanate and alcohol, involving either a direct insertion of the isocyanate into an Sn–O bond, or the organotin derivative acting as a Lewis acid.

In the former mechanism, the catalyst R_2SnX_2 reacts with the alcohol R'OH to give the tin alkoxide $R_2SnX(OR')$ or $R_2Sn(OR')_2$. The isocyanate then rapidly inserts into the Sn-O bond to give an *N*-stannylcarbamate, which rapidly react with the alcohol to give the urethane and regenerate the catalyst (Scheme 1). These individual steps can be confirmed in isolation; the insertion step is reversible.^{23,24}





The mechanisms by which the tin compound operates as a Lewis acid are suggested to be important with the tin chlorides or carboxylates which do not readily exchange their ligands with the alcohol. Three variants have been proposed. In the first two, the organotin catalyst in the above cycle is 5-coordinated as either $R_2SnX_2(HOR')$ or $R_2SnX_2(OR')^-$. Third, association of the isocyanate with R_2SnX_2 may enhance its reactivity towards nucleophilic attack by the alcohol [equation (23)].

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The masked isocyanates have been proposed to react with the glycols by either an elimination-addition or additionelimination sequence, catalysed by organotin compounds. Amides readily undergo stannylation at nitrogen, and the addition of the Sn–X bond to isocyanates is often reversible, particularly at the higher temperatures which are used for curing the paint on car bodies, and the organotin catalyst may well promote the elimination–addition route [equation (24)].

Jousseaume has shown that the difunctional tetrabutyldistannoxanes, $XR_2SnOSnR_2X$, are effective catalysts, and they may operate as binary Lewis acids, as described below.²⁵

Masked organotin catalyses have also been devised to permit the use of a one-component mixture which is stable until it is exposed to air or heat. The tetrabutyldiacyloxydistannanes are inert until they are air-oxidised to the distannoxanes when they become efficient catalysts [equation (25)].²⁶

$$ROCOBu_2SnSnBu_2COOR \xrightarrow{O_2} ROCOBu_2SnOSnBu_2COOR$$
(25)

Similarly the 2-carboxyethyltin compounds are non catalytic, but at elevated temperatures, ethene is eliminated to give the catalytic tin carboxylates [equation (26)].

$$Bu_2Sn(CH_2CH_2OCOMe)_2 \longrightarrow Bu_2Sn(OCOMe)_2 + CH_2=CH_2$$
(26)

5. Room temperature vulcanisation of silicone polymers

The third group of polymers in which the organosilicon compounds are involved are the silicones, particularly poly(dimethylsiloxane) (16) and its copolymers.

Cross-linking of the chains converts the silicone oils into elastomers with a wide variety of uses such as coatings, sealants, moulding compounds, release agents, encapsulants, and water repellents.

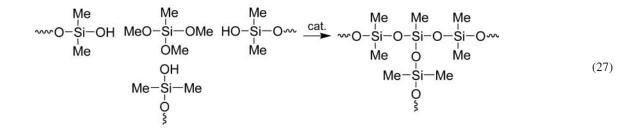
This vulcanisation can be carried out at room temperature (room temperature vulcanisation, RTV) with a tri- or tetrafunctional silane as a cross-linking agent and an organotin catalyst, which is commonly dibutyltin diacetate or dilaurate [equation (27)].

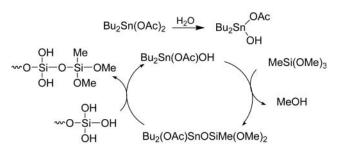
The product may be supplied in two components, one consisting of the HO- terminal polysiloxane and the other containing the tri- or tetra-methoxysilane and the organotin catalyst, and reaction occurs when the components are mixed.

A one-component product would contain a mixture of a MeO-terminal polysiloxane, the polyfunctional cross-linker, and the catalyst. When the mixture is exposed to air, the terminal MeO groups are hydrolysed to OH, and vulcanisation takes place.

A silanol-terminated silicone co-polymer can be crosslinked in the same way, and isocyanate-terminated polyurethanes can be end-capped with trialkoxysilyl groups and then subjected to vulcanisation, *e.g.* equation (28).²⁷

(MeO)₃Si(CH₂)₃NRCONH NHCONR(CH₂)₃Si(OMe)₃





Scheme 2 Mechanism of RTV of a silicone.

Silylethyl groups can be grafted onto polyethylene by treating it with the vinylsilane $(RO)_3SiCH=CH_2$ in the presence of a free radical initiator, and then these grafts can be cross-linked by hydrolysis which is catalysed by an organotin compound.

Little work has been done on the mechanism of the crosslinking, but the picture put forward by van der Weij in 1980 is generally accepted (Scheme 2).²⁸

The organotin dicarboxylate is first hydrolysed to the hydroxyl carboxylate. This reacts with the trialkoxysilane cross-linker to give a stannasiloxane, and this in turn reacts with terminal hydroxysilane groups of the polymer to cap it with a dimethoxysilane group. Repetition of this process gives a cross-linked polymer.

Jousseaume's latent distannane catalyst can also be used for curing silicones.²⁶

6. Transesterification and related reactions

Reactions at carboxyl groups, such as esterification, transesterification, transcarbamoylation, lactonisation, and ring-opening polymerisation (ROP) [equations (29–33)], are important in chemical industry.

$$(\mathsf{RCO})_2\mathsf{O} + \mathsf{R'OH} \longrightarrow \mathsf{RCO}_2\mathsf{R'} + \mathsf{H}_2\mathsf{O}$$
(29)

 $RCO_2R' + R'OH \longrightarrow RCO_2R'' + R'OH$ (30)

 $RNHCO_2R' + R"OH \longrightarrow RNHCO_2R" + R'OH$ (31)

$$HO(CH_2)_nCO_2H \longrightarrow O(CH_2)_nCO + H_2O$$
(32)

$$O(CH_2)_nCO \longrightarrow -(O(CH_2)_nCO)_m + mH_2O \quad (33)$$

These reactions can generally be catalysed by alkalis or protic acids, but frequently a less aggressive catalyst is needed because the reactants may be acid- or base-sensitive, or for avoiding corrosion of the plant, or for environmental reasons, and organotin compounds are commonly used for this purpose. This is currently a very active field of study. Dibutyltin dilaurate and dibutyltin oxide are frequently used; the latter compound is an intractable polymer, but it dissolves on reaction with the carboxyl compound to give a distannoxane, *e.g.* equation (34).

 $2Bu_2SnO + RCO_2R' \longrightarrow RCO_2Bu_2SnOSnBu_2OR'$ (34)

The dichlorodistannoxane, ClBu₂SnOSnBu₂Cl, [see equation (7)], and other difunctional distannoxanes are particularly effective, and are widely used.^{29,30} When they are used for catalysing the esterification between a carboxylic acid and an alcohol, however, the distannoxanes are immediately decomposed to give the dialkyltin diacetates, and any catalysis is by the protic acid HX which is thereby formed.³¹

Tetraphenyltin has been shown to be effective for some reactions (*e.g.* the dehydropolycondensation of *L*-lactic acid³²), but the actual catalyst is probably a triphenyltin compound, Ph₃SnX, which is formed by dephenylation. To avoid problems in recovering the organotin catalysts, polymer-supported catalysts (*e.g.* **17**)³³ and fluorous distannoxane catalysts (*e.g.* **18**)^{34,35} have been developed.³⁶

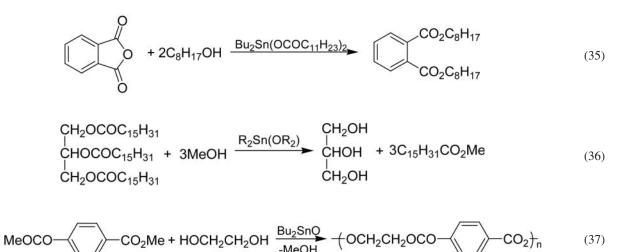
$$\begin{array}{c|c} \hline P & -(CH_2)_4 SnBuCI \\ \hline 0 & CI(C_6F_{13}C_2H_4)_2 SnOSn(C_2H_4C_6F_{13})_2 CI \\ \hline 17 & 18 \end{array}$$

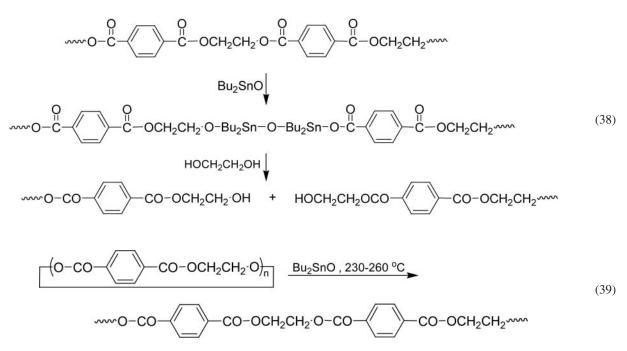
Thus dialkyl phthalates, which are used as plasticizers, can be made from phthalic anhydride and an alcohol with dibutyltin dilaurate as catalyst [equation (35)].

A simple example of transesterification is given by the reaction of methanol with palmitin, which is the main constituent of palm oil, to give methyl palmitate, which can be used in place of diesel oil in internal combustion engines [equation (36)].³⁷

Poly(ethylene terephthalate) (PET), which is used in fibres (Terylene, Dacron), or for packaging, or for blow-moulded bottles (Mylar, Melinex), can be produced by transesterification of dimethyl terephthalate with ethylene glycol [equation (37)].^{38,39}

For recycling the polymer, poly(ethylene terephthalate) (*ca* 200-mer) can be transesterified with an excess of various diols⁴⁰ at 180–270 °C over several hours in the presence of





Bu₂SnO to give an oligomer (*ca* 8–10-mer) [*e.g.* equation (38)], which can be used for recycling the polymer, or for reacting with an isocyanate for preparing a polyurethane.⁴¹ The reaction can also be carried out without solvent in a twin-screw extruder with a residence time of 1 min.⁴⁰

The waste PET polymer can also be converted into ethylene terephthalate cyclic oligomers which undergo ring-opening polymerisation (ROP) with dibutyltin oxide to regenerate the polymer [equation (39)].⁴²

Most polymers which are used in the medical field for implants, sutures, or drug-release are resorbable aliphatic polyesters formed by the ring-opening polymerisation of lactones such ε -caprolactone. This is catalysed with aluminium alkoxides or organotin alkoxides, chlorides or carboxylates, or 1,3-difunctional tetraalkyldistannoxanes [equation (40)].⁴³

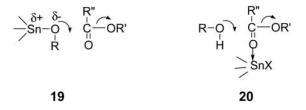
n
$$c=0$$
 $\xrightarrow{Bu_2Sn(OCOPh)_2}$ 0 (40)

Block copolymers of hydroxytelechelic poly(ethylene terephthalate) from reaction in equation (38), and carboxytelechelic poly(ε -caprolactone), can prepared with the residual organotin catalyst which is used in the glycolysis of PET [equation (38)].⁴¹

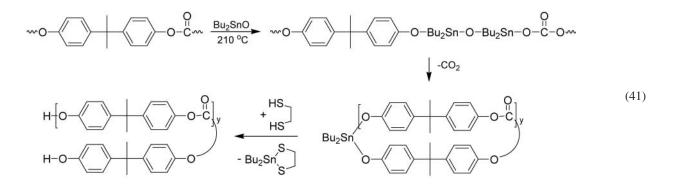
Controlled degradation of polycarbonates, which are used in CDs and DVDs, to oligocarbonates can be brought about with dibutyltin oxide. For example, poly(bisphenol-A carbonate)

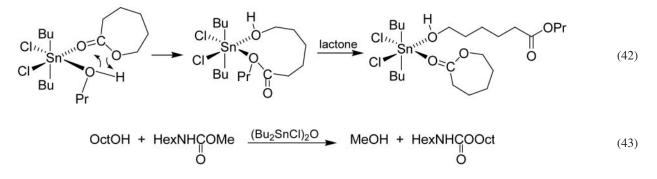
reacts with Bu_2SnO in a 10:1 molar ratio, with evolution of CO_2 , to give what are probably Bu_2Sn -containing cyclic oligocarbonates rather than linear polymers. The tin can then be removed with ethylene dithiol to give a hydroxytelechelic oligo(bisphenol-A carbonate) of one-tenth of the size of the starting polymer, and this can then be further modified [equation (41)].⁴⁴

A similar dichotomy of mechanism as in the addition to isocyanates applies to the mechanism of these substitution reactions at carboxyl groups. The organotin catalyst may react with the alcohol to give an alkoxide, enhancing the nucleophilicity of the alkoxy group (**19**), or it may react as a Lewis acid towards the carboxyl group, increasing its electrophilicity (**20**).



The former mechanism probably applies when the catalyst is introduced as the organotin alkoxide, or oxide, or carboxylate,⁴⁵ and Otera showed that in the reaction between ethanol and ethyl acetate in toluene at 100 °C the dimethoxide and the diacetate were converted into AcOBu,SnOSnBu,OEt,



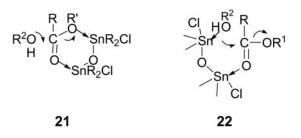


supporting this picture. The organotin chlorides, however, which do not readily undergo alcoholysis, appear to survive the reaction unchanged, and to behave as Lewis acids.

Thus for the polymerisation of ε -caprolactone by dibutyltin dichloride initiated by propanol, it was concluded that both the lactone and the alcohol coordinated to the tin, then ring-opening was brought about by nucleophilic attack of the alcohol at the acyl group of the neighbouring lactone ligand [equation (42)].⁴⁶

The situation is similar with the distannoxane catalyts. Jousseume showed that ClBu₂SnOSnBu₂Cl was recovered unchanged from the (symmetrical) transesterification of ethyl acetate with ethanol,⁴⁷ and from the transcarbamoylation of *N*hexyl *O*-methyl carbamate with octanol [equation (43)].²⁵

In both reactions, the catalyst appears to operate as a pure Lewis acid, and its efficiency derives from its nature as a double Lewis acid which can hold the two reagents in juxtaposition. Both the acyl and the alkyl oxygen atoms of the carboxylate might coordinate to the distannoxane (21), or only the acyl oxygen, with the alcohol held at the second tin centre near to the acyl carbon centre at which it reacts (22).



Dimethyl carbonate is an environmentally benign chemical with an increasing number of uses, but it is commonly prepared from phosgene, and an alternative route from carbon dioxide would obviously be better. A direct synthesis has been developed from methanol and supercritical CO₂ with dibutyltin dimethoxide as the catalyst. The water which is eliminated deactivates the catalyst, but, at 200 atm and 180 °C, if the water is removed by circulating the reactants through a molecular sieve,⁴⁸ a yield of the carbonate of about 46% can be obtained.

The water presumably hydrolyses the dimethyltin dimethoxide to the distannoxane MeOBu₂SnOSnBu₂OMe, and a mechanism which is in accord with the evidence is shown in Scheme 3.

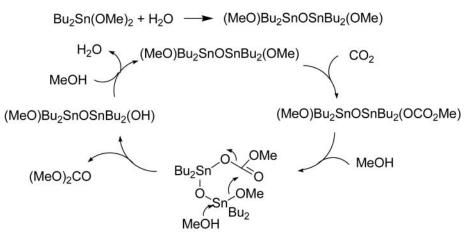
This is probably an oversimplification. The distannoxane will be present mainly as a dimer (though possibly in equilibrium with the monomer under the reaction conditions), and a decanuclear stannoxane, which may be represented as two parallel five-rung ladders, each consisting of two (Bu₂Sn)₂O units with Bu₂SnOMe units at each end, with these ladders end-bridged by two carbonate groups.⁴⁹

7. Coating glass with tin oxide

Thin films of SnO₂ deposited on various solid substrates have a variety of important applications.^{50,51,52} A layer, 1- μ m thick, fills in imperfections in the surface and strengthens the glass so that thinner bottles can be used (*e.g.* milk bottles) which use less glass and are subject to fewer breakages.

If the SnO_2 is doped with about 3% of fluoride it becomes an *n*-type semiconductior; the band gap between the filled and empty orbitals is reduced into the infrared region, making the glass transparent to solar radiation, but reflective toward heat radiation. This principle is used in designing low-emissivity window glazing (Pilkington's K glass ®), as illustrated in Fig. 1.

Doping with antimony and with indium is also common, though the latter (ITO, indium tin oxide) has a largely indium content. These semiconductors are used in a variety of electronic devices such as diodes, transistors, solar cells, heated windows, antistatic coatings, and sensors.



Scheme 3 Formation of dimethyl carbonate from methanol and CO₂:

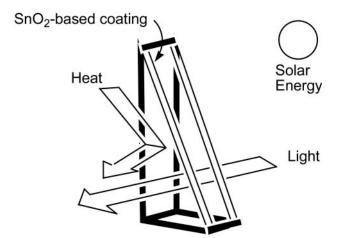


Fig. 1 Low-emissivity window double glazing.

The SnO₂ layer is usually laid down by chemical vapour deposition (CVD), where a precursor of SnO₂ is passed over the heated glass surface in the presence of air and moisture. The conditions under which this is carried out are stringent: if it is to be done on the ribbon of float glass coming off a production line at 25 cm s⁻¹, only 1–2 s are available for an even, hard, adherent field, 1000–7000 Å thick, to be deposited at about 500 °C. SnCl₄ Has often been used as the precursor of the SnO₂ in conjunction with atmospheric moisture and oxygen, but organotin compounds decompose at a lower temperature and are less aggressive, and Me₂SnCl₂ and BuSnCl₃ are preferred.

For an F-doped film, a dual source precursor may be used, the fluorine being provided by F_2 , NH_4F , HF, $BrCF_3$ or other fluorocarbons, or CF_3CO_2H . Organotin fluorides are not volatile enough to be used as single-source precursors. Fluoroalkyltin compounds are not readily available, but fluorocarboxylates such as $Bu_2Sn(OCOCF_3)_2$ are, and lose CO_2 under the operating conditions to give trifluoromethyl tin compounds.

Indium tin oxide (ITO) films are usually prepared from a dual precursor in which the indium is provided by, for example, $In(acac)_3$, which gives greater control over the In/Sn ratio than does a single precursor.

Many elementary reactions are involved in both the gas phase and on the substrate surface; for example 120 were considered in a study of the oxidation of dimethyltin dichloride,⁵³ and it is not surprising that the mechanism is not completely understood. Experimental thermochemical data on the organotin compounds is often lacking, and calculated data have to be used. The alkyltin chlorides can be used at a lower temperature than with the SnCl₄ because alkyl-Sn bonds are weaker than Sn–Cl bonds.

The model for the mechanism for the CVD of SnO_2 from $BuSnCl_3$ and O_2 which seems most in accord with experiment is that in which $BuSnCl_3$ reacts with absorbed oxygen, whereas, when water is present, O_2 in the vapour phase reacts with an adsorbed $BuSnCl_3$ -H₂O complex.⁵⁴

8. Marine antifouling⁵⁵

Sea-going vessels accumulate on their hulls a coating of marine organisms such as seaweed, barnacles, and tubeworms which produce drag and drastically reduce the efficiency of propulsion of the vessel. A graphic illustration of a fouled hull is given on the cover of de Mora's book.⁵⁶ The amount of fuel consumed can be increased by 40%, and the ship has to be dry-docked to clean the hull.

Fouling of naval ships and submarines increases their acoustic signature and renders them easier to detect by sonar, and in 1997 it was estimated that the US navy spent \$100 million a year on dealing with fouling.

In the 1960s, tributyltin and triphenyltin compounds (oxide, chloride, acetate, *etc.*) were introduced, replacing the copper oxide which had been used previously to reduce the growth of fouling. The organotin compound was incorporated into the hull paint ("free association paints"), and slowly diffused out, providing protection for 18–24 months. During that period, the rate of release declined as antifoulant had to diffuse to the surface from deeper in the paint.

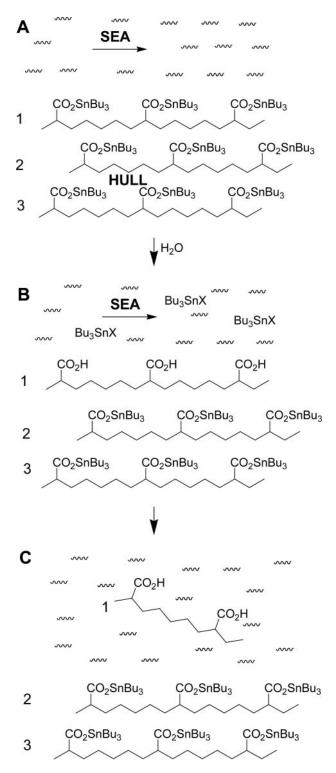


Fig. 2 Mode of action of self-polishing antifouling coatings.

190 JOURNAL OF CHEMICAL RESEARCH 2010

In 1974, ablative self-polishing paints were introduced, and their mode of action is illustrated in Fig. 2. They contained a copolymer of, typically, methyl methacrylate and tributylstannyl methacrylate (Fig. 2A), designed to leach tributyltin at a constant rate of 1.6 μ g cm⁻² per day. The resulting acrylic acid (Fig. 2B) copolymer is hydrophilic and is ablated off by the motion of the ship, exposing a fresh tin acrylate surface (Fig. 2C), and a steady release of Bu₃SnX can be achieved. When the ship is stationary in harbour, the rate of leaching is much less. The paint provided protection for 5 to 7 years, and the hull did not need cleaning before repainting. In 1987, the amount of tributyltin compounds used in antifouling paints in 1987 was reported to be about 450 tons.

However, the tributyltin which was released into the water turned out to be toxic to shellfish and molluscs such as oysters. The use of these paints was progressively restricted in the 1980s and a ban on their use came into effect in January 2008, but the technology that was developed is now being adapted to the design of self-polishing copper polyacrylates which work on the same principle.

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